Effect of Adding Boron on the Electrical Conductivity of Alloy AL-Mg-Mn

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ABSTRACT

Boron treatment is widely used to remove transition metals Ti, V and Zr for electrical conductive grade (Al), addition of boron in aluminum melts significantly decreases these impurities (as solute), boron can combine with even trace amounts of transition elements to form insoluble boride compounds thus lowering the transition metal impurity content in the metal, the borides can then be separated by precipitation, add boron leads to a significantly improvement in the electrical conductivity of the aluminum commercial, studies shown that mechanisms of reactions between boron and transition metal impurities in liquid aluminum are not fully understood. The effects of artificial aging treatment at temperature (175°C) and different times (1-5-10-20-30-50 hr.) on electrical conductivity for alloy used in the current search and the action mechanism have been investigated, as the percentage of improvement in the electrical conductivity (23.6%) of the alloy (B6) at temperature (175°C) and aging time (20 hr.) compared with the alloy base (A).

Keywords: boron, electrical conductivity, artificial aging, homogenization, transition metals.

1. INTRODUCTION

Aluminum can be used as an electrical conductor if the level of impurities controlled precisely, in particular, the concentration of transitional metals Ti, Zr, V, and Cr. Their effect is minimized when they are in a combined form rather than in solution with aluminum, commercially, boron treatment has been used to remove transition metal elements through the formation of borides [1]. This is carried out by adding aluminum boron master alloys [2,3]. The main use of Al-B master alloys is to improve the electrical conductivity. Also it is widely used as a grain refiner of aluminum alloys, especially aluminum casting alloys [4,5].

Addition of B in Al melts significantly decreases these impurities (as solute) to several parts per million (ppm) even when the original concentrations are already low [6,7]. B can combine with even trace amounts of transition elements to form insoluble boride compounds [8] thus lowering the transition metal impurity content in the metal [7, 9, 10]. The borides can then be separated by settling. This treatment is particularly beneficial for purifying Al which contains a total of less than 0.05 wt% of the transition metals. While this process is particularly effective for removing Ti, V and Zr, it has substantially no effect on the removal of other common impurities such as Fe, Si and Cu [11, 12, 13]. The process has been found to be useful in treating commercial Al of a purity of 99.4% and higher [11]. Cooper and Keams [14] studied and demonstrated the removal of transition metal impurities from Al-melts to produce a higher electrical conductivity grade Al alloy [8].

Shingu et al. [15] obtained a high-purity Al fraction from Al containing both eutectic impurities (such as Fe, Si, Cu and Mg) and peritectic impurities (such as Ti, V and Zr) by adding boron to Al melt and rotating an immersed cooling body in the melt. The cooled immersed body surface crystallized high purity AL. The peritectic impurities reacted with the boron to form metallic borides, which were centrifugally forced away from the cooling body by rotation. The eutectic impurities were removed from the crystallized Al on the surface based on the principle of solute partitioning and subsequent segregation. The final cast Al block was found to contain 0.008 wt% Fe, 0.012 wt% Si, <0.0001 wt% Ti, 0.0002 wt% V, <0.0002 wt% Zr and 0.0003 wt% of B [15].

Although boron treatment is widely used in industry, the detailed mechanisms of reactions between boron and transition metal impurities in liquid Al are not fully understood. Moreover, the exact nature of the borides type, their morphology and composition need to be analyzed to get a full
understanding of borides formation mechanism for effective boron treatment of Al [11].

In this work, researcher investigate the effect of boron addition on the electrical conductivity of aluminum alloy by studying chemical composition of alloy formed by boron and transition element impurities.

2. EXPERIMENTAL

This section deals with melting and casting operations and the preparation of test samples alloy (A,B) used in the current research.

The table (2.1) includes a Chemical Analysis of Alloy used in the Current Search

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mg</th>
<th>Mn</th>
<th>Fe</th>
<th>Si%</th>
<th>Cu</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti%</th>
<th>Pb</th>
<th>V</th>
<th>Sn</th>
<th>Ni</th>
<th>B</th>
<th>Zr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>A</td>
<td>0.627</td>
<td>0.348</td>
<td>0.319</td>
<td>0.14</td>
<td>0.07</td>
<td>0.01</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>Rem</td>
<td>0.0028</td>
<td>0.0973</td>
<td>Rem</td>
</tr>
<tr>
<td>B</td>
<td>0.352</td>
<td>0.283</td>
<td>0.314</td>
<td>0.14</td>
<td>0.05</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0035</td>
<td>0.0498</td>
<td>Rem</td>
<td></td>
</tr>
</tbody>
</table>

Underwent several heat treatment of the alloy (A, B) included:

- Homogenizing treatment (500°C) and time (10hr).
- Solution heat treatment (500°C) and time (1hr).
- Artificial Ageing at isothermal ageing temperature (175°C) and different times (1-5-10-20-30-50 hr.) after solution treatment.

This work also included electrical conductivity test, which was conducted simultaneously with heat treatments. Weighed pieces of aluminum, according to the quantities corresponding elements of alloying to get the required percentages weighted, taking into consideration the case of oxidation that you get to the elements during the casting therefore the added an extra quantity of elements with high ability oxidation (B). For melting, the components of alloys were used electric oven type (MARIO DIMAIO-20122 MILANO No.5332 - Italy) works in the field (0-1350°C). The process of melting and casting includes ingot melting (A) prepared in advance in graphite crucibles capacity (1kg) and then added boron powder which is wrapped in aluminum foil to prevent oxidation when contact with molten, and then remove the slag resulting from the smelting process, where the cleaner has been added slag (CaCo3) and repellent before casting process gases few minutes, then molten move by ceramic rod in order to avoid pollution of the molten any is the elements required to ensure melting and molten homogeneity. Finally complete the casting process very rapidly in metal molds that have been pre-heated to temperatures of up to (200-300°C) to avoid solidification of molten quickly when touching the wall of the mold and get rid of the cold casting defects.

2.1 Homogenizing Treatment

Conducted treatment homogenizing to get rid of whimsical formative semi dissolved and rich impurities deposited on the border crystalline, conducting such treatment develop castings inside a container filled with powder alumina to reduce oxidation and develop the container. In turn electric oven works in the field (0-1200°C), then samples were cooled inside the oven slow cooling to room temperature, and the table (2.2) shows the homogenizing treatment conditions.

Table (2.2) Homogenizing treatment conditions for samples electrical conductivity

<table>
<thead>
<tr>
<th>Alloy code</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1, B1</td>
<td>Homog. at (500 °C) for (10hr) + R.T</td>
</tr>
</tbody>
</table>

Homg. = Homogenization.
R.T = Room Temperature.

2.2 Specimens Preparation

After the end of treatment homogenizing been cutting castings to samples in the form of tablets in diameter (30mm) and thickness (9mm), then conducted the process of grinding of the samples for the purpose configured to operations of measuring electrical conductivity, and began the process of grinding using paper grinding of carbide silicon with gradients (180-400-600-800-1000-1200-1500-2000-3000), then the polishing process was conducted using a mechanical polishing device used in this process alumina powder, water, and after the end of each stage of the smoothing or polishing samples washed with distilled water and dried hot air stream.
2.3 Solution Heat Treatment

After homogenizing treatment was conducted solution heat treatment samples electrical conductivity by placing the samples in the same furnace used for the treatment of homogenizing. This treatment included following steps:

- Developing samples within furnace and heating to a temperature of (500°C).
- Keeping the samples at temperature (500°C) for a period of (1hr).
- Directed by samples from the furnace too quickly extinguished with water.

Table (2.3) Solution heat treatment conditions and quenching for the samples electrical conductivity

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₂,B₂</td>
<td>S.H.T at (500 °C) for (1hr) + W.Q</td>
</tr>
</tbody>
</table>

W.Q = Water Quenching.

2.4 Artificial Aging treatment

Conducted artificial aging treatment of alloy samples at a constant temperature (175°C) included:

- Solution heat treatment conducted at temperature (500°C) and the period of stay (1hr).
- Quenching of the samples with cold water and as quickly as possible.
- Samples heating at a temperature (175°C) and different times (1, 5, 10, 20, 30, 50 hr.)

Table (2.4) Artificial Aging Treatment Conditions for Samples Electrical Conductivity for Different Times

<table>
<thead>
<tr>
<th>Alloy code</th>
<th>conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₃,B₃</td>
<td>Homog. at (500 °C) for (10hr) + R.T + S.H.T at (500 °C) for (1hr.) + W.Q + Aging at (175 °C) for (1hr.)</td>
</tr>
<tr>
<td>A₄,B₄</td>
<td>Homog. at (500 °C) for (10hr) + R.T + S.H.T at (500 °C) for (1hr.) + W.Q + Aging at (175 °C) for (5hr.)</td>
</tr>
<tr>
<td>A₅,B₅</td>
<td>Homog. at (500 °C) for (10hr) + R.T + S.H.T at (500 °C) for (1hr.) + W.Q + Aging at (175 °C) for (10hr.)</td>
</tr>
<tr>
<td>A₆,B₆</td>
<td>Homog. at (500 °C) for (10hr) + R.T + S.H.T at (500 °C) for (1hr.) + W.Q + Aging at (175 °C) for (20hr.)</td>
</tr>
<tr>
<td>A₇,B₇</td>
<td>Homog. at (500 °C) for (10hr) + R.T + S.H.T at (500 °C) for (1hr.) + W.Q + Aging at (175 °C) for (30hr.)</td>
</tr>
<tr>
<td>A₈,B₈</td>
<td>Homog. at (500 °C) for (10hr) + R.T + S.H.T at (500 °C) for (1hr.) + W.Q + Aging at (175 °C) for (50hr.)</td>
</tr>
</tbody>
</table>

2.5 Electrical Conductivity Test

This test conducted using samples in the form of discs with a diameter (30mm) and thickness (9mm) and all alloys used in this research before and after conditions were used of heat treatment, and this is considered test indicative of changes in the physical properties and mechanical installation and the microstructure, has been conducting this using a device type (SIGMASCOPE® SMP 10) by (Standard measurement according to ASTM E 1004 and DIN EN 2004-1.), the measured electrical conductivity is expressed as a percentage of the International Annealed Copper Standard (IACS%), were performed all conductivity tests at room temperature. The test instrument was calibrated using copper standards, prior to commencement as well as during the conductivity measurements.

In addition, every point on the charts represents the relationship between conductivity - time rate for five readings or more to different regions of the sample and from both sides of the sample, has been drawing the relationship between the values of electrical conductivity and time for different conditions through which alloys to know the behavior of alloys by different thermal transactions.
3. RESULTS

3.1 Electrical conductivity

Electrical conductivity was measured for the samples before and after conduct transactions thermal and periodically as a measure of the changes taking place and found that the alloy (B) has the highest electrical conductivity compared with other alloys (A), as shown in the table (3.1) which represents the electrical conductivity readings for the samples.

<table>
<thead>
<tr>
<th>Code name</th>
<th>A</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
<th>A7</th>
<th>A8</th>
</tr>
</thead>
<tbody>
<tr>
<td>condition</td>
<td>as</td>
<td>H</td>
<td>H+</td>
<td>1hr.</td>
<td>5hr.</td>
<td>10hr.</td>
<td>20hr.</td>
<td>30hr.</td>
<td>50hr.</td>
</tr>
<tr>
<td>IACS%</td>
<td>39.7</td>
<td>42.6</td>
<td>41.3</td>
<td>43.7</td>
<td>43.4</td>
<td>43.2</td>
<td>41.9</td>
<td>41.5</td>
<td></td>
</tr>
<tr>
<td>Code name</td>
<td>B</td>
<td>B1</td>
<td>B2</td>
<td>B3</td>
<td>B4</td>
<td>B5</td>
<td>B6</td>
<td>B7</td>
<td>B8</td>
</tr>
<tr>
<td>condition</td>
<td>as</td>
<td>H</td>
<td>H+</td>
<td>1hr.</td>
<td>5hr.</td>
<td>10hr.</td>
<td>20hr.</td>
<td>30hr.</td>
<td>50hr.</td>
</tr>
<tr>
<td>IACS%</td>
<td>44.7</td>
<td>48.9</td>
<td>48.5</td>
<td>48.1</td>
<td>47.3</td>
<td>47.8</td>
<td>49.1</td>
<td>48.9</td>
<td>46.4</td>
</tr>
</tbody>
</table>

H + S = Homogenization + Solution Heat Treatment.

The figures (3.1),(3.2) shows effect of aging time on electrical conductivity for the alloys (A),(B) at temperature (175°C) and for different times.
Fig (3.2) Effect aging time on electrical conductivity for alloy (B) at temperature (175°C) for different times

Fig (3.3) Effect of aging time on electrical conductivity for the Alloys (A, B) at temperature (175°C) and for different times
4. DISCUSSION

4.1 Effect of homogenizing treatment on the electrical conductivity of the alloys

Homogenizing treatment conducted to eliminate textural phases similarities dissolved and rich precipitates impurities on the grain boundaries where samples were heated to a temperature of (500^\circ C) and the stay time (10 hr.) after that the samples were cooled inside the oven with slow cooling to room temperature. Most aluminum alloys are typically subjected homogenization heat treatment after casting [16]. The objectives of homogenization are to eliminate micro segregation, reduce manganese in solid solution and obtain desirable size and distribution of constituent particles including fine dispersions and coarse primary particles, which have a strong influence on the recrystallization kinetics, texture development, grain size and mechanical properties of the alloy [16, 17].

Table (3.1) shows the values of the electrical conductivity of the alloys (A, B) before and after conduct heat treatment, we note that the value of the electrical conductivity of the alloy (B) after a homogenizing treatment temperature (500^\circ C) and stay time (10 hr.) is (48.9 IACS\%) compared with the electrical conductivity of the alloy (A), which amounted to (42.6 IACS\%) under the same conditions. The percentage of improvement in the electrical conductivity of the alloy (B) after a homogenizing treatment (14.7\%) compared with the alloy (A), this is due to the fact that the electrical conductivity of the alloy monotonously increases with increasing homogenization temperature and time [18]. When the alloy is heated to (350 ^\circ C), the (EC) starts to increase with increasing temperature, indicating that the supersaturated solid solution starts to decompose, the (EC) of the alloy gets a maximum at about (500 ~ 530 ^\circ C), then it decreases with increasing temperature, which indicates the increasing of (Mn) content in the solid solution with increasing temperature, this is due to the dissolution of dispersions caused by the increase of solubility of (Mn) in solid solution. During homogenization at (600 ^\circ C), the (EC) increases with holding time, the (α) dispersions dissolve quickly into the matrix, while the Al6 (Mn, Fe) dispersions grow quickly at the expense of the (α) dispersions [16, 17]. The depletion of the matrix solid solubility decreases the ability of electron scattering in the alloy, resulting in the electrical conductivity increased [18]. The essential explanation for the different values of the electrical conductivity of the alloy through homogenizing treatment pointed out by the researcher [18] depending on mathiessen theory to calculate the electrical resistance of the alloy as follows:

\[ \rho = \rho_0 + \Delta \rho_s + \Delta \rho_g + \Delta \rho_d + \Delta \rho_v + \Delta \rho_d + \Delta \rho_v \]

Where:

\[ \Delta \rho_s = \text{electrical resistance caused by the solid soluble atoms.} \]

\[ \Delta \rho_p = \text{electrical resistance caused by the precipitated phase.} \]

\[ \Delta \rho_v = \text{electrical resistance caused by the vacancy.} \]

\[ \Delta \rho_g \& \Delta \rho_d = \text{electrical resistance caused by the grain boundaries and dislocations, respectively.} \]

Many researches [19, 20, 21] have pointed out that the most influencing factor for electrical resistance is \( \Delta \rho_s \), follows by \( \Delta \rho_p, \Delta \rho_g, \Delta \rho_v \) and \( \Delta \rho_d \). This is because the scattered ability to electron caused by the solute atoms that distort the aluminum matrix lattice is much greater than that caused by others, such as the precipitate phases. In the condition of direct chill casting, most of Mg, Mn, Sc and Zr elements are solution in the aluminum matrix, which raises \( \Delta \rho_s \), so the conductivity of the alloy is very low. During homogenization, supersaturated solid solution is decomposed and Al1(Sc, Zr) and Al6Mn particles precipitated. Thus, the solid solution depletes and \( \Delta \rho_s \) greatly decreases. At the same time, the precipitation of Al1(Sc, Zr) and Al6Mn particles causes additional scattering and gives the increment of the electrical resistance, \( \Delta \rho_p \), but in the whole, the electrical conductivity of the alloy will increase along with the precipitation of Al13(Sc, Zr) and Al6Mn.

4.2 Effect of artificial aging treatment on electrical conductivity

Fig. (3.3) effect of aging time on the electrical conductivity of the alloy (A, B) at a temperature (175 ^\circ C) and for different times, and the note from the figure that the electrical conductivity of the alloy (B) is the highest compared with alloy (A), where the values of electrical conductivity are (43.9, 49.1 IACS\%) of the alloys (A, B) respectively. The ratio of improvement in the conductivity of the alloy (A4) at aging time (5 hr.) is (10.6\%) compared with the electrical conductivity of the alloy (A), and alloy (B6) at aging time (20 hr.) is (9.8\%) compared with the electrical conductivity of the alloy (B), either alloy (B6) was the ratio improvement in the electrical conductivity is (11.8\%) compared with the electrical conductivity of the alloy (A4), while the percentage of improvement in the electrical conductivity of the alloy (B) compared with alloy (A) is (23.6\%) . The behavior of alloy in terms of increased conductivity because electrical conductivity increases with increasing ageing time. The reason of the increase in electrical conductivity is thought to be the purification of the matrix by means of segregation of the solute atoms and formation of semi-coherent metastable phase. As the rate of precipitation is accelerated, the foreign atoms that act as scattering centers of electrons segregate from the aluminum matrix at an enhanced rate. Equilibrium precipitates are larger particles and increase in size as ageing proceeds, thus
minimizing their scattering effect[22]. The behavior shown by alloy (A,B) through the process of aging artificial temperature (175 °C) shown in fig.(3.3) where we note an increase in the electrical conductivity of the alloy followed by stabilization in the values of conductivity. Studies in this field that there are two opposite effects contribute to the variations in electrical conductivity. The annihilation of vacancies during the recovery and the decrease of dislocation density during the recrystallization increase conductivity, on the other hand, the dissolution of soluble precipitate phases (i.e. Mg removing to solution) decreases conductivity[23,24]. Going back to fig. (3.3) note that the alloy (A) shows an increase in electrical conductivity by (10%) after (1 hr.) of aging to stabilize after the conductivity values of this alloy, the difference in electrical conductivity between the as - cast and maximum value is 2.4 MS m-1 (4.2 IACS%) at aging temperature (175 °C), while other researchers pointed[25] that difference in electrical conductivity between the as-cast and maximum value for Al-0.1%Zr at aging temperature (425-450°C) is 3.6 ± 0.1 MS m-1 (6.1 IACS%).

The effect of presence zirconium in the alloy (B), refers to the research results reached by the Willey’s Divided into two groups the first one is the influence of the presence of zirconium in the solid solution, which causes a significant decrease of aluminum's resistivity, and the other is its presence in the precipitates (intermetallic phase Al3Zr). According to Willey, the Zr influence in the solid solution equals 17 nm/% mass, and in the precipitates – only 0.4 nm/% mass[26].

The role played by the (Zr) through its presence in a solid solution (Al3Zr) is to reduce the electrical resistance, which results in an increase in the electrical conductivity of the alloy.

Fig. (3.3) shows that the alloy (B) shows an increase in conductivity which is increases by (7.6%) during the aging time (1 hr.) to stabilize after the electrical conductivity with increasing aging time.

That alloy (Ca) has the highest conductivity (49.1 IACS %) at the time of aging (20 hr.) is attributable to the role of boron in increasing the electrical conductivity of the alloy. Boron treatment is widely used to remove transition metals Ti, V and Zr for electrical conductive grade (Al) ,addition of (B) in (Al) melts significantly decreases these impurities (as solute) to several parts per million (ppm) even when the original concentrations are already low , (B) can combine with even trace amounts of transition elements to form insoluble boride compounds thus lowering the transition metal impurity content in the metal . The borides can then be separated by precipitation. While this process is particularly effective for removing Ti, V and Zr, it has substantially no effect on the removal of other common impurities such as Fe, Si and Cu [27]. The main use of Al-B master alloys is to improve the electrical conductivity. In addition, it is widely used as a grain refiner of aluminum alloys, especially aluminum casting alloys[28].

The process has been found to be useful in treating commercial (Al) of a purity of (99.4%) and higher[27]. This is different to what researcher reached where boron was added to alloy (B) containing commercial aluminum of a purity is less than (99.4%).

Al-B alloy has primarily two stable phases as (AlB12) and (AlB2), AlB2 has hexagonal closed packed crystal structure, whereas (AlB12) has tetragonal crystal structure[29].

Boron has been added by (3%) to alloy (A) to produce alloy (B) for the purpose of improving the electrical conductivity through the combination of boron with the trace amounts of transition elements (V, Ti, Cr, Zr) to form insoluble compounds, note that the maximum ability for soluble boron in aluminum is (0.022%)[30], and by noting table (2.1) which shows the chemical analysis of alloys, we find lower ratios weighted transition elements (V,Ti,Cr,Zr) when adding boron to the alloy (A).

The reactions depend upon diffusion of the impurities in the aluminum melt and the availability of boron/aluminum borides. It has been reported that these reactions of boron with transition metals are fast enough that 70% of increase in electrical conductivity is achieved in the first couple of minutes, further increase in electrical conductivity is quite slow and takes more than two hours, i.e. after the heavy boride particles settle at the bottom of furnace, studies have shown that solution thermodynamics and the detailed reaction mechanisms of the borides formed in aluminum melts are not well understood[31].

5. CONCLUSIONS

1. The main use of Al-B master alloys is to improve the electrical conductivity.

2. Add boron improves electrical conductivity for commercial aluminum by combining with trace amounts of transition elements (Ti, V & Zr) to form insoluble boride compounds.

3. In a time when treatment of boron effective for removing transition elements Ti, V and Zr, it has substantially no effect on the removal of other common impurities such as Fe, Si and Cu.

4. Add boron to the alloy (A) Led to improve the electrical conductivity of the alloy (B) by (23.6%).

5. Given homogenizing treatment at temperature (500 °C) and time (10 hr.) superiority clear for alloy (B) in the value of the electrical conductivity which amounted to (48.9 IACS%) compared with the electrical conductivity of the alloys (A) which amounted to (42.6% IACS%) , as the ratio of
improvement in the electrical conductivity (14.7\%) of the alloy (B1) compared with alloy (A1).

6. Showed artificial aging treatment conducted at temperature (175 °C) and different times improvement in the values of electrical conductivity of the alloys (A,B) compared with the values of the electrical conductivity of the alloy as is cast.

Acknowledgement

Researcher would like to thank the Iraqi Ministry of Electricity and training and development office of the same ministry and Ms. Amira, head of development for granting me the opportunity to complete my studies and for their continued support throughout the period of research, as well as thanks go to all employees of the metal Materials Engineering Laboratory at the University of Babylon.

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